

# PATENT ABSTRACTS OF JAPAN

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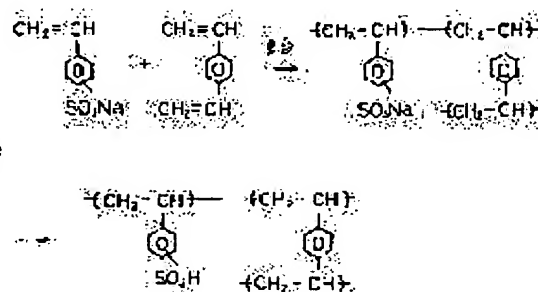
(72)Inventor : KATO MITSUAKI

## (54) GAS DIFFUSION ELECTRODE FOR SOLID POLYMER ELECTROLYTE MEMBRANE TYPE FUEL CELL AND ITS MANUFACTURING METHOD

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide an electrode for solid polymer electrolyte membrane type fuel cells capable of enhancing the characteristics of the electrode by securing continuous proton conduction paths while securing more triphasic interfaces serving as electrode reaction sites, and resultantly capable of economically enhancing the output performance of a fuel cell incorporating this electrode.

**SOLUTION:** This gas diffusion electrode equipped with catalyst layers for sandwiching between them a solid polymer electrolyte membrane of the solid polymer electrolyte membrane type fuel cell is characterized in that the catalyst layers contain a compound made by introducing a proton-conductive functional group into a hydrocarbon resin.



## LEGAL STATUS

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CLAIMS

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[Claim(s)]

[Claim 1] The gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed in the gas diffusion electrode equipped with the catalyst bed which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell.

[Claim 2] The manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by consisting of a process which mixes and distributes the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed in the manufacture approach of the gas diffusion electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell, and a process which carries out the polymerization of this monomer and carries out macromolecule quantification.

[Claim 3] The manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by consisting of the process which sets to the manufacture approach of the electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell, and mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, a process which carries out the polymerization of this monomer and carries out macromolecule quantification, and a process to which a proton conductivity functional group is introduced into said macromolecule.

[Claim 4] Said proton conductivity functional group is the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by being chosen from the acid radical which consists of a sulfonic acid, a carboxylic acid, phosphonic acid, and phosphoric acid, and its manufacture approach.

[Claim 5] Said hydrocarbon system resin Polystyrene, ABS plastics, SB resin, an AS resin, AES resin, a styrene divinylbenzene copolymer, a polycarbonate, Polyethylene terephthalate, polyarylate, polysulfone, polyether sulphone, A polyphenylene sulfide, polyamidoimide, a polyamide, polyimide, The gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by being polymers which consist of carbon and hydrogen at least, such as a polyether, a polyether ketone, a polyether ether ketone, and polybenzimidazole, and its manufacture approach.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrode for solid-state polyelectrolyte membrane type fuel cells, and its manufacture approach.

[0002]

[Description of the Prior Art] In order to cope with the environment and resource problem in earth scales, such as CO<sub>2</sub> effluent control for an air pollution control, and a petroleum-resources exhaustion, conventionally, it is clean and energy density is high, as for the solid-state polyelectrolyte mold fuel cell which the charging time makes unnecessary, it is most brought into the limelight, and researches and developments are furthered at a quick pace in each country in the world including Japan.

[0003] A polymer electrolyte fuel cell is equipment which acquires the electromotive force produced in that case by being characterized by having the solid-state polyelectrolyte film of proton conductivity as the component part, and making fuel gas and oxidation gas, such as hydrogen, react electrochemically.

[0004] The electrode reaction at the time of hydrogen gas being used for a fuel cell as fuel gas, and oxygen being used for it as oxidation gas is  $2H_2 \rightarrow 4H^{++} + 4e^-$  at an anode pole side. Reaction formula The proton which the reaction which becomes one occurred and was generated passes along the inside of a solid-electrolyte membrane, and is  $4H^{++} + O_2 + 4e^- \rightarrow 2H_2O$  in a cathode pole. Reaction formula The reaction which becomes two occurs and electromotive force arises among two poles.

[0005] By the way, at the present stage, some technical problems which must be conquered are still left behind to utilization of a fuel cell.

[0006] The presentation of a current electrode catalyst bed becomes carbon black from the ingredient and perfluorocarbon-sulfonic-acid system proton conductivity ingredient which supported the platinum which is a catalyst, the catalyst presentation which kneaded these is applied to base materials, such as carbon paper, and the gas diffusion electrode is formed as shown in a U.S. Pat. No. 4876115 number official report or JP,3-208260,A.

[0007] Being formed from the gas diffusion electrode which made the catalyst bed mixture of the styrene divinylbenzene sulfonic acid type resin which is the solid-state polyelectrolyte film at moreover, addition and the electrode characteristic of the ion-exchange resin to electrochemistry, 53, No.10, and the oxygen pole joined to a p812-817(1985) "solid-state polyelectrolyte (Nafion)", and the carbon powder which supported the catalyst metal, the styrene divinylbenzene sulfonic-acid-type-resin powder which is a proton conductor and a polystyrene binder is indicated.

[0008]

[Problem(s) to be Solved by the Invention] However, in a U.S. Pat. No. 4876115 number official report or JP,3-208260,A, if it must be made for the proton conductivity ingredient in the gas diffusion electrode of a fuel cell not to have to melt into water and there are many functional groups of proton conductivity, it will become water solubility, therefore since a perfluorocarbon-sulfonic-acid system proton conductivity ingredient cannot enlarge ion exchange capacity, the migration of a proton to an electrolyte membrane becomes rate-limiting, and it cannot take out sufficient current.

[0009] moreover, although ion exchange capacity can be make larger than a perfluorocarbon sulfonic acid system proton conductivity ingredient about electrochemistry, 53, No.10, and p812-817 (1985), since a proton conductor be a powder, the poor contact of a powder particle arise by the defect of a powder particle etc., the function cannot fully demonstrate, but so it become rate-limiting move [ of a proton ] it, even a solid-state polyelectrolyte film do not reach and a proton cannot take out sufficient current.

[0010] thus, the proton generated in the three-phase zone on a catalyst (a hydrogen gas phase, a catalyst

phase, conductive matter phase) since ion exchange capacity of a Prior art was not large in the proton conductor in a catalyst bed being a powder configuration -- up to the solid-state polyelectrolyte film -- proton conduction -- moving in the inside of the body becomes rate-limiting, consequently sufficient current cannot be taken out. Therefore, in order to raise the output engine performance of a fuel cell, it is necessary to raise the property of this proton conductor.

[0011] Although the platinum catalyst and the perfluorocarbon-sulfonic-acid system proton conduction ingredient are used for the catalyst bed of this basic presentation and it has become the factor of high cost, as for the platinum catalyst, the possibility of low-cost-izing with the technique of recycle and amount[ of low / used ]-izing is left behind.

[0012] however, perfluorocarbon-sulfonic-acid resin with a very expensive proton conduction ingredient -- base -- this is solution-ized in a raw material and it is manufactured. It is an ingredient expensive as much as platinum, and that cost is used as an ingredient of each development manufacturer company mainstream of a fuel cell stack and a gas diffusion electrode current [ many ], and low-cost-izing of a fuel cell is difficult for it as [ this ]. Therefore, a proton conductor needs to be low-cost-ized.

[0013] this invention offers the electrode for solid-state polyelectrolyte membrane type fuel cells and fuel cell which can boil markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode, and can raise it in order to secure a continuous proton tract, securing more three-phase zones which are what solved the above-mentioned technical problem, and are electrode reaction sites.

[0014]

[Means for Solving the Problem] Invention of claim 1 made in order to solve the above-mentioned technical technical problem is a gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed in the gas diffusion electrode equipped with the catalyst bed which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell.

[0015] it is possible to offer the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode, and can raise it by invention of claim 1 since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites.

[0016] Invention of claim 2 made in order to solve the above-mentioned technical technical problem be the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterize by to consist of a process which mix and distribute the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed , and a process which carry out the polymerization of this monomer and carry out macromolecule quantification in the manufacture approach of the gas diffusion electrode which pinch the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell .

[0017] it is possible to offer the manufacture approach of the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode, and can raise it by invention of claim 2 since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites.

[0018] Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

[0019] Invention of claim 3 made in order to solve the above-mentioned technical technical problem sets to the manufacture approach of the electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane-type fuel cell, and is the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane-type fuel cells which consists of the process which mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, a process which carries out the polymerization of this monomer and carries out macromolecule quantification, and a process to which a proton conductivity functional group is introduced into said macromolecule.

[0020] Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

[0021] Invention of claim 4 made in order to solve the above-mentioned technical technical problem is the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by choosing said proton conductivity functional group from the acid radical which consists of a sulfonic acid, a carboxylic acid, phosphonic acid, and phosphoric acid, and its manufacture approach.

[0022] By invention of claim 4, the effectiveness of making proton conductivity discover can be offered.

[0023] Invention of claim 5 made in order to solve the above-mentioned technical problem Said hydrocarbon system resin Polystyrene, ABS plastics, SB resin, an AS resin, AES resin, a styrene divinylbenzene copolymer, a polycarbonate, Polyethylene terephthalate, polyarylate, polysulfone, polyether sulphone, A polyphenylene sulfide, polyamidoimide, a polyamide, polyimide, They are the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells according to claim 1 to 3 characterized by being polymers which consist of carbon and hydrogen at least, such as a polyether, a polyether ketone, a polyether ether ketone, and polybenzimidazole, and its manufacture approach.

[0024] The effectiveness that a polymer can be made from a monomer and a proton conductivity functional group can be introduced by invention of claim 5 can be offered.

[0025]

[Embodiment of the Invention] Hereafter, this invention is explained with reference to a drawing.

[0026] After this invention mixes and distributes the monomer of the compound which introduced the proton conductivity functional group into the hydrocarbon system resin which is a proton conductor at a catalyst bed, its property of an electrode improves by carry out the polymerization of the monomer, carry out macromolecule quantification and produce in the catalyst bed of the gas diffusion electrode for polymer electrolyte fuel cells which consists of polytetrafluoroethylene which is a repellent a catalyst support carbon particle, proton conductivity material, or if needed in order to secure a continuous proton tract, secure more three-phase zones which are electrode reaction sites. it is invention which can boil markedly the output engine performance of the fuel cell combined with this electrode as a result, and can raise it.

[0027] This gas diffusion electrode is a gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed.

[0028] In the manufacture approach of the gas diffusion electrode which pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell, the manufacture approach of the manufacture approach of the gas diffusion electrode is carried out from the process which mixes and distributes the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed, and the process which carries out the polymerization of this monomer and carries out macromolecule quantification.

[0029] Moreover, as other manufacture approaches, the manufacture approach is carried out from the process which mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, the process which carries out the polymerization of this monomer and carries out macromolecule quantification, and the process to which a proton conductivity functional group is introduced into said macromolecule.

[0030] Here, the acid radical which consists of that of a sulfonic acid, a carboxylic acid, phosphonic acid, and phosphoric acid is introduced as a proton conductivity functional group. Among these, it is desirable to make a sulfonic group into an indispensable functional group. because, as hydrocarbon system resin used for the proton conductor which is because it has the effectiveness of the dissociation constant of a proton being high and having high proton conductivity Polystyrene, ABS plastics, SB resin, an AS resin, AES resin, a styrene divinylbenzene copolymer, A polycarbonate, polyethylene terephthalate, polyarylate, Polymers, such as polysulfone, polyether sulphone, a polyphenylene sulfide, polyamidoimide, a polyamide, polyimide, a polyether, a polyether ketone, a polyether ether ketone, and polybenzimidazole, are mentioned.

[0031] There is especially no limit in the approach of introducing this functional group into hydrocarbon system resin. It is better to compound the resin which introduces a functional group and has a functional group, after carrying out the polymerization of the monomer and making it macromolecule resin like the reaction formula of drawing 4, but to compound the macromolecule resin which has a functional group by carrying out a polymerization like [ it is desirable and ] the reaction formula of drawing 3, after introducing a functional group into a resin monomer.

[0032] The reason is that it is easier to introduce into a monomer rather than it introduces a functional group into a polymer.

[0033] There is especially no limit about the approach of making this proton conductor forming into a catalyst bed. After mixing and distributing a resin monomer in catalyst bed components, such as a catalyst support carbon particle, and coating a resin monomer on the catalyst bed which the catalyst bed was formed, and carried out the polymerization of the monomer, carried out giant-molecule quantification or was formed, the polymerization of the monomer may be carried out and giant-molecule quantification may be carried out.

[0034] (Example 1) As shown in drawing 1 (a), the dispersion undiluted solution (Daikin Industries, LTD.,

- POLYFLOND1 grade) whose poly TERORA fluoro ethylene (PTFE) particle content concentration is 60% was diluted with water so that PTFE concentration might become 15% of the weight. Carbon paper CP with a thickness of 180 micrometers (the Toray Industries, Inc. make, TGP-060) was dipped into this solution. [0035] Then, the above-mentioned carbon paper CP was picked out from the solution, in 80-degree-C atmospheric air, after desiccation ( drawing 1 (b)), it held for 390 degree-Cx 60 minutes, PTFE was sintered ( drawing 1 (c)), and the carbon paper given a water-repellent finish was obtained ( drawing 1 R> 1 (d)). [0036] As shown in drawing 2 , platinum concentration carried out homogeneity distribution of the platinum support carbon (product [ made from Johnson MASSEI ], HISPEC4000) 15g which is 40 % of the weight into methanol 115g and 115g of water. [0037] Subsequently, 10g [ of sodium styrenesulfonate ] and divinylbenzene (DVB) 1g and azobisisobutyronitril (ABIN) 0.1g were added into this solution, it mixed and distributed, and the catalyst paste was obtained ( drawing 2 ). In addition, the above-mentioned reaction formula is expressed with the reaction shown in drawing 3 . [0038] The catalyst bed was formed so that the amount of platinum support might become 0.2 mg/cm<sup>2</sup> to water-repellent-finish carbon paper with a doctor blade method about this catalyst paste. Then, after the air dried, it held for 80 degree-Cx 8 hours, and the polymerization of the monomer was carried out. Next, after washing several times with water, it dipped in the sulfuric-acid water solution of 0.5 mol/l, the sulfonic group was exchanged for H mold, and the gas diffusion electrode was obtained ( drawing 1 (e)). [0039] The polyelectrolyte film compounded and obtained by the approach of the following [ this gas diffusion electrode ] was inserted, 8 MPa, the heat press was carried out for 5 minutes, and 150 degrees C of membrane electrode zygotes were produced. [0040] After irradiating the gamma ray of 20kG(ies) in nitrogen and under ordinary temperature at the Pori (ethylene tetrafluoroethylene) film of 50 micrometers of thickness, the graft of the styrene chain was carried out to Pori (ethylene tetrafluoroethylene) by dipping a film at 60 degrees C into the mixed solution of styrene monomer:divinylbenzene:xylene =95:5:30 (volume section) for 2 hours. 50 degrees C was dipped after drying a film for 1 hour during mixing of the chlorosulfonic acid 30 volume section and the 1 and 2-dichloroethane 100 volume section. The film after desiccation was washed by 90-degree C new deionized water for 2 hours. The chemical formula (polystyrene sulfonate graft-Pori (ethylene-TETORO fluoro ethylene)) of the film is shown in drawing 7 . [0041] Next, this membrane electrode zygote was attached to the fuel cell single cel, and generation-of-electrical-energy evaluation was carried out. Evaluation conditions used air as the cel temperature of 75 degrees C, and oxidizer gas, and used pure hydrogen as fuel gas, and these utilization factors supplied both gas pressure by 0.25MPa(s) 40% and 80% respectively. Under the present circumstances, in oxidizer gas, the steam of 0.22 was supplied and humidified by the mole ratio to hydrogen capacity at 0.04 and fuel gas to the air content by the mole ratio. The evaluation result is shown in drawing 5 R> 5. [0042] (Example 2) The catalyst bed was formed so that it might become the amount of platinum of an example 1 and the amount same by the same approach at the same water-repellent-finish carbon paper as an example 1 about the catalyst paste which carried out homogeneity distribution of the same platinum support carbon 15g as an example 1 into isopropyl alcohol 115g and 115g of water. [0043] Then, spreading and desiccation were repeated in several steps on the catalyst bed front face in which the solution which added 10g [ of sodium styrenesulfonate ] and divinylbenzene 1g and azobisisobutyronitril 0.1g into methanol 100g, and was mixed and distributed was formed on water-repellent-finish carbon paper. Then, it held for 80 degree-Cx 8 hours, the polymerization of the monomer was carried out, and the gas diffusion electrode was obtained. [0044] The membrane electrode zygote was produced on the same conditions as an example 1, and generation-of-electrical-energy evaluation of the same electrolyte membrane as an example 1 and the above-mentioned electrode was carried out on the same evaluation conditions as an example 1. The evaluation result is shown in drawing 5 . [0045] (Example of a comparison) Homogeneity distribution of the same platinum support carbon 15g as an example 1 and the 180g (the Asahi Chemical Co., Ltd. make, SS-1080) of 5% of the weight of the ion-exchange-resin solutions was carried out into isopropyl alcohol 24g and 24g of water, and the catalyst paste was obtained. The catalyst bed was formed in the same water-repellent-finish carbon paper as an example 1 so that it might become the amount of platinum of an example 1 and the amount same by the same approach, and the gas diffusion electrode was obtained. In addition, the chemical formula of the above-mentioned ion exchange resin consists of a chemical formula shown in drawing 6 . [0046] Nafion112 (product made from Du Pont) was used for the macromolecule electrolysis film, 2 MPa,



the heat press was carried out for 5 minutes, the membrane electrode zygote was produced, and 120 degrees C carried out generation-of-electrical-energy evaluation on the same evaluation conditions as an example 1. The evaluation result is shown in drawing 5.

[0047] drawing 5 is a graph showing the relation between output voltage and current density, and is understood from this graph -- as -- an example 1 and an example 2 -- in all, as compared with the example of a comparison, output voltage is high. it is thought that this reason boils markedly the output engine performance of the fuel cell which it can improve, consequently is low cost and combined the property of an electrode with this electrode in order to secure a continuous proton tract, securing more three-phase zones which are electrode reaction sites, and raises it.

[0048]

[Effect of the Invention] In the gas diffusion electrode equipped with the catalyst bed to which invention of the 1st of this invention pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell Since it is the gas diffusion electrode characterized by containing the compound which introduced the proton conductivity functional group into hydrocarbon system resin in said catalyst bed Since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites, the property of an electrode can be improved. By consequently, low cost it is possible to offer the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell combined with this electrode, and can raise it.

[0049] In the manufacture approach of a gas diffusion electrode that furthermore invention of the 2nd of this invention pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell The process which mixes and distributes the monomer which introduced the proton conductivity functional group into hydrocarbon system resin at a catalyst bed, Since it is the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by carrying out the polymerization of this monomer and consisting of a process which carries out macromolecule quantification Since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites, the property of an electrode can be improved. By consequently, low cost it is possible to offer the manufacture approach of the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell combined with this electrode, and can raise it. Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

[0050] In the manufacture approach of an electrode that furthermore invention of the 3rd of this invention pinches the solid-state polyelectrolyte film of a solid-state polyelectrolyte membrane type fuel cell The process which mixes and distributes the monomer of hydrocarbon system resin at a catalyst bed, and the process which carries out the polymerization of this monomer and carries out macromolecule quantification, Since it is the manufacture approach of the gas diffusion electrode for solid-state polyelectrolyte membrane type fuel cells characterized by consisting of a process to which a proton conductivity functional group is introduced into said macromolecule Since a continuous proton tract is secured, securing more three-phase zones which are electrode reaction sites like the 2nd above-mentioned invention, the property of an electrode can be improved. By consequently, low cost it is possible to offer the manufacture approach of the electrode for solid-state polyelectrolyte membrane type fuel cells which can boil markedly the output engine performance of the fuel cell combined with this electrode, and can raise it. Moreover, this manufacture approach is liquefied, and since it has solidified after mixing and distributing at a catalyst bed, it has the advantage that a continuous proton tract can be formed.

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[Translation done.]

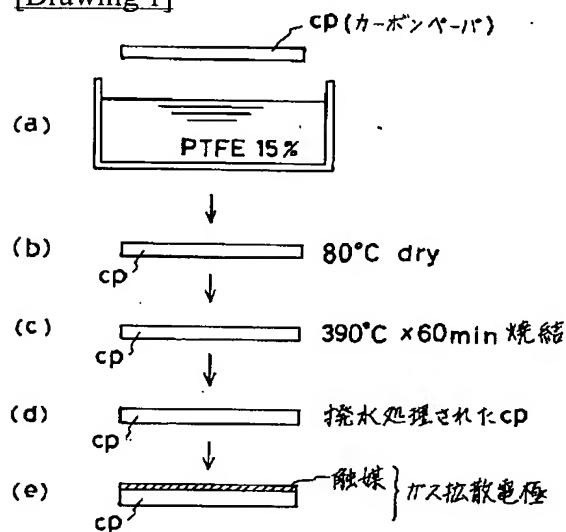
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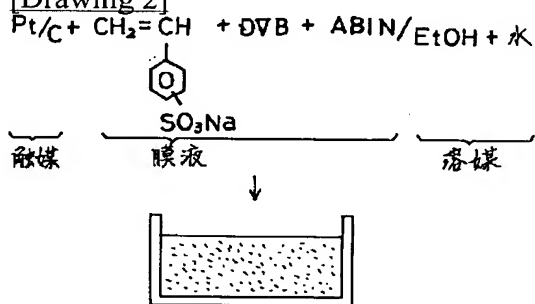
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## DRAWINGS

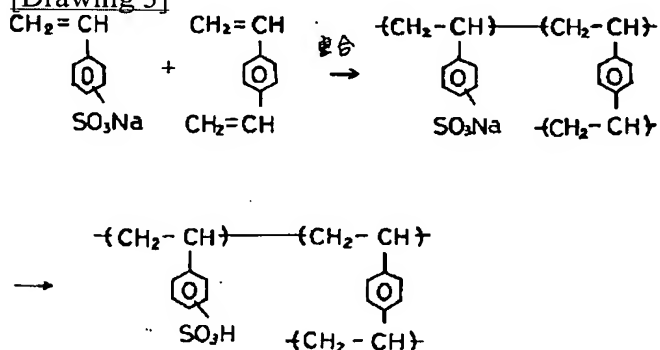
[Drawing 1]



[Drawing 2]

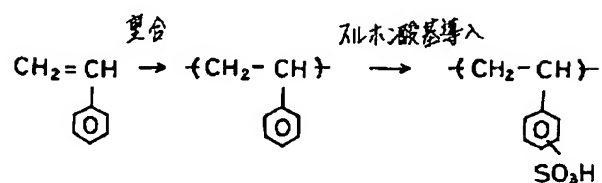


[Drawing 3]

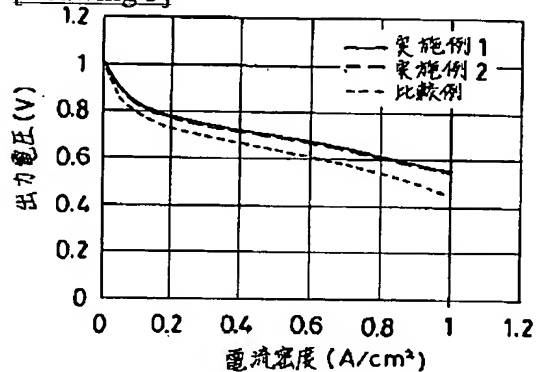


[Drawing 4]

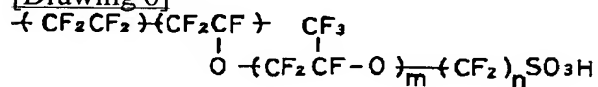




[Drawing 5]

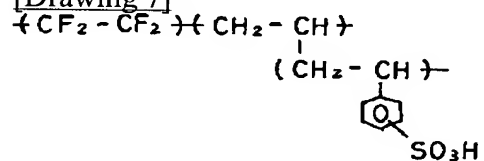


[Drawing 6]



$m = 0 \text{ or } 1$   
 $n = 2 \sim 5$   
 $x = 1.5 \sim 14$

[Drawing 7]



[Translation done.]

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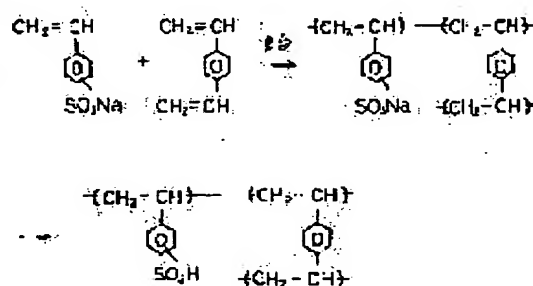
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(72)Inventor : KATO MITSUAKI

**(54) GAS DIFFUSION ELECTRODE FOR SOLID POLYMER ELECTROLYTE MEMBRANE TYPE FUEL CELL AND ITS MANUFACTURING METHOD****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide an electrode for solid polymer electrolyte membrane type fuel cells capable of enhancing the characteristics of the electrode by securing continuous proton conduction paths while securing more triphasic interfaces serving as electrode reaction sites, and resultantly capable of economically enhancing the output performance of a fuel cell incorporating this electrode.

**SOLUTION:** This gas diffusion electrode equipped with catalyst layers for sandwiching between them a solid polymer electrolyte membrane of the solid polymer electrolyte membrane type fuel cell is characterized in that the catalyst layers contain a compound made by introducing a proton-conductive functional group into a hydrocarbon resin.



(19) 日本国特許庁 (JP) (12) 公開特許公報 (A)

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(P2002-334702A)  
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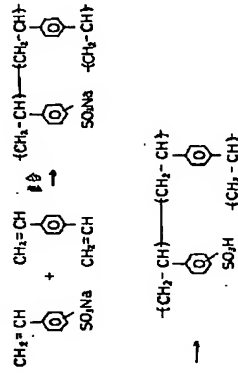
(5) Int. Cl. <sup>7</sup>	識別記号	F I	特許請求の範囲
H 01 M	4/86	4/86	4/86
H 01 M	4/88	4/88	4/88
H 01 M	8/10	8/10	8/10

審査請求 未請求 請求項の数 5 O L (全 6 頁)

(21) 出願番号	特開2001-137476 (P2001-137476)	(71) 出願人	000000011 アイシン精機株式会社
(22) 出願日	平成13年5月8日 (2001.5.8)	(72) 発明者	加藤 充明 愛知県刈谷市朝日町2丁目1番地 アイシン 精機株式会社内 愛知県刈谷市朝日町2丁目1番地 アイシン 精機株式会社内
Fターム(参考)	5H018 A06 AS02 AS03 B012 B016 C06 D008 E03 E05 E07 5H026 A06 B008 B010 C04 C05 E018		

(54) 【発明の名称】 固体高分子電解質型燃料電池用ガス拡散電極及びその製造方法。

(57) 【要約】  
【課題】 電極反応サイトである三相界面をより多く確保しつつ連続的なプロトン伝導経路を確保するため電極の特性が向上することができ、その結果、低コストで、この電極と組み合わせた燃料電池の出力性能を格段に向上させることができる固体高分子電解質型燃料電池用電極を提供する。  
【解決手段】 固体高分子電解質型燃料電池の固体高分子電解質膜を挟持する触媒層を備えたガス拡散電極において、炭化水素系樹脂にプロトン伝導性官能基を導入した化合物を前記触媒層に含有したことを特徴とするガス拡散電極。



【特許請求の範囲】

【請求項1】 固体高分子電解質型燃料電池の固体高分子電解質膜を挟持する触媒層を備えたガス拡散電極において、炭化水素系樹脂にプロトン伝導性官能基を導入した化合物を前記触媒層に含有したことを特徴とするガス拡散電極。

【請求項2】 固体高分子電解質型燃料電池の固体高分子電解質膜を挟持するガス拡散電極の製造方法において、炭化水素系樹脂にプロトン伝導性官能基を導入したモノマーを触媒層に混合・分散する工程と、該モノマーを重合し高分子量化する工程とからなることを特徴とする固体高分子電解質型燃料電池用ガス拡散電極の製造方法。

【請求項3】 固体高分子電解質型燃料電池の固体高分子電解質膜を挟持する電極の製造方法において、炭化水素系樹脂のモノマーを触媒層に混合・分散する工程と、該モノマーを重合し高分子量化する工程と、前記高分子にプロトン伝導性官能基を導入する工程とからなることを特徴とする固体高分子電解質型燃料電池用ガス拡散電極の製造方法。

【請求項4】 前記プロトン伝導性官能基は、スルホン酸、カルボン酸、ホスホン酸、燐酸からなる酸基から選ばれることを特徴とする請求項1～請求項3記載の固体高分子電解質型燃料電池用ガス拡散電極及びその製造方法。

【請求項5】 前記炭化水素系樹脂は、ポリスチレン、ABS樹脂、SB樹脂、AS樹脂、AES樹脂、スチレンジビニルベンゼン共重合体、ポリカーボネート、ポリ

メタクリレート、生成したプロトンは固体電解質膜の\*30\*中を通り、カソード極で、  
 $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

なる反応が起こり、両極間に起電力が生ずる。  
【0005】 ところで、現段階では、燃料電池の實用化には、また克服しなければならない幾つかの課題がまだ残されている。

【0006】 米国特許 4876115 号公報あるいは特開 3-208260 号公報に示されているように、現在の燃料電池の組成は、カーボンブラックに触媒である白金を担持した材料、パーフルオロカーボン系スルホン酸系プロトン伝導性材料からなり、これらを混練した触媒組成をカーボンペーパーなどの基材に塗布し、ガス拡散電極が形成されている。

【0007】 また、電気化学、53、No. 10、p. 812～817 (1985) 「固体高分子電解質 (Nafion) に接合する酸基層へのイオン交換樹脂の添加とその電極特性」には、固体高分子電解質であるスチレンジビニルベンゼン系スルホン酸樹脂と、触媒金属を担持したカーボン粉末とプロトン伝導体であるスチレンジビニルベンゼン系スルホン酸樹脂粉末とポリスチレン結合剤との混合物を触媒層としたガス拡散電極とから形成され

【発明の詳細な説明】

エチレンテレフタレート、ポリアリレート、ポリスルホン、ポリエーテルスルホン、ポリフェニレンスルフィド、ポリアミドイミド、ポリアミド、ポリイミド、ポリエーテル、ポリエーテルケトン、ポリエーテルエーテルケトン、ポリベンゾイミダゾール等の少なくとも2種以上を重合してなる重合体であることを特徴とする請求項1～請求項3記載の固体高分子電解質型燃料電池用ガス拡散電極及びその製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、固体高分子電解質膜型燃料電池用電極及びその製造方法に関する。

【0002】

【従来の技術】 従来、大気汚染防止のためのCO2排出規制及び石油資源枯渇といった地球規模での環境・資源問題に対処するため、クリーンでエネルギー密度が高く、充電時間が不要とする固体高分子電解質型燃料電池は最も脚光を浴びられ、日本を始め世界中の各国で急ピッチに研究開発が進められている。

【0003】 固体高分子電解質型燃料電池は、プロトン伝導性の固体高分子電解質膜をその構成部品として有することを特徴としており、水素等の燃料ガスと酸化ガスを電気化学的に反応させることによって、その際に生ずる起電力を得る装置である。

【0004】 燃料電池は、燃料ガスとして水素ガスを、酸化ガスとして酸素を用いた際の電極反応は、アノード極側では、

反応式 1  
アノード極側では、  
 $2H_2 \rightarrow 4H^+ + 4e^-$

反応式 2  
カソード極側では、  
 $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

【0008】

【発明が解決しようとする課題】 しかしながら、米特許 4876115 号公報あるいは特開 3-208260 号公報において、燃料電池のガス拡散電極中のプロトン伝導性材料は水に溶けやすいようにしなければならず、プロトン伝導性の官能基が多くあると水溶性になり、従って、パーフルオロカーボン系スルホン酸系プロトン伝導性材料は、イオン交換容量を大きくすることができないため、電解質膜へのプロトンの移動が促進となり十分な電流を取り出せない。

【0009】 また、電気化学、53、No. 10、p. 812～817 (1985) に関しては、パーフルオロカーボン系スルホン酸系プロトン伝導性材料よりイオン交換容量を大きくすることができ、プロトン伝導性が粉末であるため、粉末粒子の欠陥等で粉末粒子の接触不良が生じ、その機能が十分に発揮できず、それゆえ、プロトンの移動が促進となり、プロトンが固体高分子電解質膜まで到達せず、十分な電流を取り出せない。

【0010】このように、従来の技術は、触媒層中のプロトン伝導体が粉未形状であったり、イオン交換容量が大きくなために、触媒上の三相界面（水素ガス相、触媒相、伝導体物質相）で発生したプロトンが固体高分子電解質膜までプロトン伝導体中を移動する事が困難となり、その結果、十分な電流を取り出せない、よって、燃料電池の出力性能を向上させるには、このプロトン伝導体の特性を向上させる必要がある。

【0011】この基本組成の触媒層には白金触媒、パーフルオロカーボンポリマー系プロトン伝導材料が使用されており、高コストの要因になっているが、白金触媒はリサイクルと低使用量の技術での低コスト化の可能性が残されている。

【0012】しかしながら、プロトン伝導材料は、極めて高価なパーフルオロカーボンポリマー系樹脂を原料として、これを溶媒化して製造されている。そのコストは白金並みに高価な材料であり、現在、多くの燃料電池スタック及びガス拡散電極の間接メーカー各社主流の材料として使用され、このままでは、燃料電池の低コスト化が困難である。従って、プロトン伝導体の低コスト化が必要である。

【0013】本発明は、上記課題を解決したもので、電極反応サイトである三相界面をより多く確保しつつ連続的なプロトン伝導路を確保するため電極の特性が向上することができ、その結果、低コストで、この電極と組み合わせた燃料電池の出力性能を格段に向上させることが可能な固体高分子電解質型燃料電池用電極及び燃料電池を提供するものである。

【0014】課題を解決するための手段 上記課題を解決するためになされた請求項1の発明は、固体高分子電解質型燃料電池の固体高分子電解質膜を挟持する触媒層を備えたガス拡散電極において、炭化水素系樹脂にプロトン伝導性官能基を導入した化合物を前記触媒層に含有したことを特徴とするガス拡散電極である。

【0015】請求項1の発明により、電極反応サイトである三相界面をより多く確保しつつ連続的なプロトン伝導路を確保するため電極の特性が向上することができ、その結果、低コストで、この電極と組み合わせた燃料電池の出力性能を格段に向上させることができる。固体高分子電解質型燃料電池用電極を提供することが可能である。

【0016】上記技術的課題を解決するためになされた請求項2の発明は、固体高分子電解質型燃料電池の固体高分子電解質膜を挟持するガス拡散電極の製造方法において、炭化水素系樹脂にプロトン伝導性官能基を導入したモノマーを触媒層に混合・分散する工程と、該モノマーを重合し高分子量化する工程とからなることを特徴とする固体高分子電解質型燃料電池用ガス拡散電極の製造方法である。

【0017】請求項2の発明により、電極反応サイトに三相界面をより多く確保しつつ連続的なプロトン伝導路を確保するため電極の特性が向上することができ、その結果、低コストで、この電極と組み合わせた燃料電池の出力性能を格段に向上させることができる。固体高分子電解質型燃料電池用電極の製造方法を提供することが可能である。

【0018】また、この製造方法は液体状触媒層に混合・分散したのち、固体化している為、連続的なプロトン伝導路を形成することができるという利点がある。

【0019】上記技術的課題を解決するためになされた請求項3の発明は、固体高分子電解質型燃料電池の固体高分子電解質膜を挟持する電極の製造方法において、炭化水素系樹脂のモノマーを触媒層に混合・分散する工程と、該モノマーを重合し高分子量化する工程と、前記高分子にプロトン伝導性官能基を導入する工程とからなる固体高分子電解質型燃料電池用ガス拡散電極の製造方法である。

【0020】また、この製造方法は液体状触媒層に混合・分散したのち、固体化している為、連続的なプロトン伝導路を形成することができるという利点がある。

【0021】上記技術的課題を解決するためになされた請求項4の発明は、前記プロトン伝導性官能基は、スルホン酸、カルボン酸、ホスホン酸、燐酸からなる酸基を選択されることを特徴とする請求項1～請求項3記載の固体高分子電解質型燃料電池用ガス拡散電極及びその製造方法である。

【0022】請求項4の発明により、プロトン伝導性を発現させるという効果を奏することができる。

【0023】上記技術的課題を解決するためになされた請求項5の発明は、前記炭化水素系樹脂は、ポリスチレン、ABS樹脂、SB樹脂、AS樹脂、AES樹脂、ポリエチレンテレフタレート、ポリアリレート、ポリスチレン、ポリエチレンテレフタレート、ポリアリレート、ポリイミド、ポリエーテルケトン、ポリエーテルエーテルケトン、ポリエーテルスルホン、ポリフェニレンスルホン、ポリエーテルスルホン、ポリイミド、ポリイミド、ポリエーテルケトン、ポリエーテルエーテルケトン、ポリエーテルスルホン等の少なくとも二種と水素とからなる重合体であることを特徴とする請求項1～請求項3記載の固体高分子電解質型燃料電池用ガス拡散電極及びその製造方法である。

【0024】請求項5の発明により、モノマーから重合体を作ることができ、かつプロトン伝導性官能基を導入することができるという効果を奏することができる。

【0025】【発明の実施の形態】 以下、本発明について図面を参照して説明する。

【0026】本発明は、触媒担持カーボン粒子、プロトン伝導性材料あるいは必要に応じて撥水材であるポリテトラフルオロエチレンからなる固体高分子型燃料電池用ガ

イングした後、そのモノマーを重合し高分子量化してよい。

【0034】（実施例1）図1（a）に示すように、ポリテトラフルオロエチレン（PTFE）粒子含有濃度が60%のディスパージョン原液（ダイキン工業株式会社、POLYFLON D1 グレード）をPTFE濃度が15重量%になるように水で希釈した。この溶液中に厚さ80μmのカーボンペーパー（東レ株式会社、TP-GP-060）を浸した。

【0035】続いて上記カーボンペーパー-C-Pを溶液から取り出し、80℃水中で乾燥後（図1（b））、90℃×60分保持しP-P-Eを焼結し（図1（c））、撥水処理されたカーボンペーパーを得た（図1（d））。

【0036】図2に示すように、白金濃度が40重量%の白金担持カーボン（ジョンソンマッセイ社製、HIS-PEC4000）15gをメタノール115g、水115g中に均一分散した。

【0037】次いで、この溶液中にスチレンスルホン酸ソーダ10g、ジビニルベンゼン（DVB）1g、アゾビスイソブチロニトリル（ABIN）0.1gを加え混合・分散し、触媒ペーストを得た（図2）。なお上記化学反応式は図3に示す反応で表される。

【0038】この触媒ペーストを撥水処理カーボンペーパーにドクターブレード法により白金担持量が0.2mg/cm<sup>2</sup>になるように触媒層を形成した。続いて風乾後、80℃×8時間保持し、モノマーを重合した。次に水にて数回洗浄したのち、0.5mol/lの硫酸水溶液に浸しスルホン酸基をH型に交換し、ガス拡散電極を得た（図1（e））。

【0039】このガス拡散電極で以下の方法で合成して得られた高分子電解質膜を挟み、150℃、8MPa、5分間加熱プレスし、膜電極接合体を作製した。

【0040】膜厚50μmのポリ（エチレン-テトラフルオロエチレン）フィルムに20kGyのγ線を照射し、常温下で照射した後、フィルムをスチレンモノマー：ジビニルベンゼン：キジレン＝95：5：30（容積部）の混合溶媒中に60℃で2時間浸すことにより、ポリ（エチレン-テトラフルオロエチレン）にスチレン鎖をグラフトした。フィルムを乾燥後、クロスリンクを30容積部と1、2-ジクロロエタン100容積部の混合中に、50℃、1時間浸した。乾燥後の膜を90℃の新しい脱イオン水で2時間洗浄した。その膜の化学式（ポリスチレンスルホン酸グラフトポリ（エチレン-テトラフルオロエチレン））を図7に示す。

【0041】次に、この膜電極接合体を燃料電池セルに組み付け発電評価した。評価条件はセル温度75℃、酸化剤ガスとして空気、燃料ガスとして純水素を用い、これらの利用部が各々40%、80%、ガス圧は1、0.25MPaで供給した。この際、酸化剤ガスには空

気量に対しモル比で0.04、燃料ガスには水素ガス量に対しモル比で0.22の水蒸気を供給し加温した。図5にその評価結果を示す。

【0042】(実施例2) 実施例1と同じ白金担持カーボン15gをイソプロピルアルコール115g、水115g中に均一分散した触媒ペーストを、実施例1と同じ洗浄処理カーボンペーストに実施例1と同じ方法で同じ量の白金量となるように触媒層を形成した。

【0043】続いて、メタノール100g中にステレンスルホン酸ソーダ10g、ジニルベンゼン1g、アソビスイソプロパリール0.1gを加え混合・分散した溶液を、洗浄処理カーボンペースト上に形成した触媒層表面に数回に分けて塗布・乾燥を繰り返した。その後、80℃×8時間保持し、モノマーを重合しガス拡散電極を得た。

【0044】実施例1と同じ電解質膜と上記電極を実施例1と同じ条件で膜電極接合体を作製し、実施例1と同じ評価条件で発電評価した。図5にその評価結果を示す。

【0045】(比較例) 実施例1と同じ白金担持カーボン15gと5重量%のイオン交換樹脂溶液(旭化成株式会社、SS-1080)180gをイソプロピルアルコール24g、水24g中に均一分散し触媒ペーストを得た。実施例1と同じ洗浄処理カーボンペーストに実施例1と同じ方法で同じ量の白金量となるように触媒層を形成し、ガス拡散電極を得た。なお上記イオン交換樹脂の化学式は図6に示される化学式からなる。

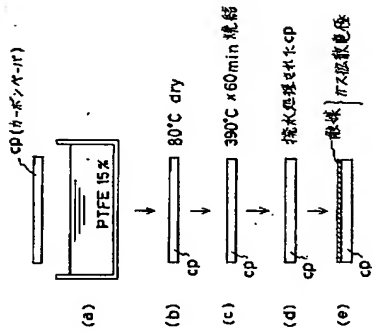
【0046】高分子電解質Nafion<sup>®</sup>112(DuPont製)を用い、120℃、2MPa、5分間熱プレスし、膜電極接合体を作製し、実施例1と同じ評価条件で発電評価した。図5にその評価結果を示す。

【0047】図5は、出力電圧と電流密度との関係を表すグラフで、このグラフからわかるように、実施例1及び実施例2いずれも比較例と比較して出力電圧が高くなっている。この理由は電極反応サイトである三相界面をより多く確保しつつ連続的なプロトン伝導路を確保するため電極の特性が向上することができ、その結果、低コストで、この電極と組み合わせた燃料電池の出力性能を格段に向上させると考えられる。

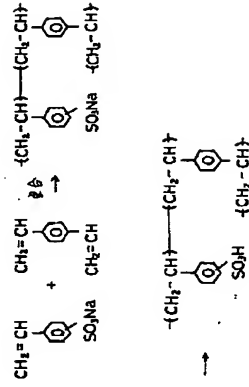
【0048】

【発明の効果】 本発明の第1の発明は、固体高分子電解質型燃料電池の固体高分子電解質膜を支持する触媒層を備えたガス拡散電極において、炭化水素系樹脂にプロトン伝導性官能基を導入した化合物を前記触媒層に含有したことを特徴とするガス拡散電極であるので、電極反応サイトである三相界面をより多く確保しつつ連続的なプロトン伝導路を確保するため電極の特性が向上することができ、その結果、低コストで、この電極と組み合わせ

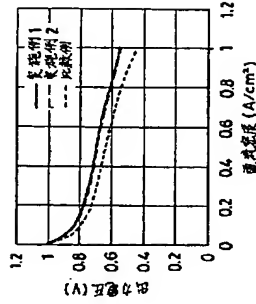
【図1】



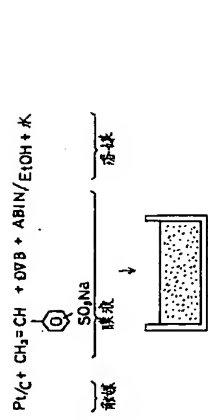
【図3】



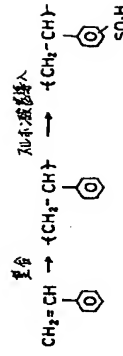
【図5】



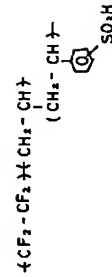
【図2】



【図4】



【図7】



【図6】

